CHEMISTRY AND STRUCTURE OF COALS: EVALUATION OF ORGANIC STRUCTURE
BY COMPUTER AIDED DIFFUSE REFLECTANCE INFRARED SPECTROSCOPY.{*}

E. L. Fuller, Jr., N. R. Smyrl, R. L. Howell, and C. S. Daw{**}

Plant Laboratory, Y-12 Plant, Box Y, Oak Ridge, TN 37830{***}

INTRODUCTION
Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy
has become a very informative method of evaluating the chemistry and
structure of coals, chars, and related materials {1,2,3}. Infrared
spectroscopy has long been recognized as an informative means of
studying the chemistry and physics of coals {4,5}. Recent advances
in instrumentation, computer assistance, and techniques have apprecia-
bly enhanced the amount and caliber of the spectra and the scientific
importance of the conclusions{6,7}. The enhanced sensitivity of these
new instruments has permitted renewed interest in nondestructive spec-
troscopic studies by diffuse reflectance infrared spectroscopy{8,9}.

EXPERIMENTAL
The spectrometer, cell, and techniques for measuring the diffuse re-
flectance spectra of solid samples over a wide range of temperatures
and pressures have been described previously {1,2,10,11}. A portion of
this study is devoted to extending our capabilities to be able to
study unperturbed solid surfaces of rather large pieces of coal and
to directly monitor changes wrought in simulated chemical and physical
processing. Grinding of coals is known to alter the chemical and
physical structure of coals and although DRIFT studies require much
less stringent treatment{9} there is most assuredly some modification
due to the energy dissipation accompanying percussive grinding{12}.
The coal sample for this study was a "run of the mine" aliquot taken
from the -3/+4 mesh seive fraction, sealed in a glass bottle and
stored for approximately two months, free from thermal effects
(drying) and extensive oxidation (weathering) which are known to
markedly alter the morpholgy and chemistry of both the organic and the
inorganic (mineral) constituents in coals{13}. This sample was
provided by the Tennessee Valley Authority from the Paradise
(Kentucky) Mine and is generally ranked as High Volatile C-Bituminous
as representative of the feed stock for the fluidized bed combustion
facility.

RESULTS AND DISSCUSION
Typically the cleaved surfaces (parallel to the bedding plane) vary in
appearance due to the heterogeneous distribution of the macerals in
the structure. The variation in reflection of visible light allowed us
to focus on glossy or dull areas of the surface of the piece of coal
and to note the variation in DRIFT response over distances greater
than our beam size (ca. 2mm with our 6X condensing optics). Figure 1
shows the variation in DRIFT signal. Spectrum A was taken with the
incident beam flooding a visibly homogenous region of high reflectiv-
ity and we note that there is appreciable specular reflection in the
infrared with little or no spectral features indicative of diffuse
reflection. The negative features (500 and 1100 cm-1) are undoubtedly

due to anomolous despersion or reststrahlen effects{14,15} which are
regarded as detrimental to DRIFT analyses and allow us to deduce some
information concerning the physical state (consolidation) of the coal
structure in this region. In marked contrast we note appreciable
difference when sampling and dull area of the same piece of coal. The
DRIFT spectrum, spectrum B, is still of very poor quality due to the
consolidated nature of the substrate. Very good DRIFT spectra can be
obtained after gentle abrasion of the surface with fine grit "Emory
Paper" and removal of the dislodged material as shown in Spectrum C of
Figure 1. This mild abrasion forms a surface which is rough enough to
reflect and absorb electromagnetic radiation much as a fine powder.
This spectral response is virtually identical to that of powders of
similar rank, given that the quantitative nature varies due to
chemistry and structure of individual aliquots. These spectra in turn
correlate quite well with their counterparts obtained in the trans-
mission mode after encapsulsation in KBr or some other support medium.

Figure 2 serves to show that one can use the DRIFT technique to
monitor chemical and physical changes of a given sample of coal very
well. Spectrum D shows the DRIFT response of the same area of the same
sample in vacuum at 400 C after exposure to oxygen gas at 400 C long
enough to attain the steady state conditions deduced by sensing no
further change in spectral features (intensities, band shapes and
intensties) with time. Visual observation allows one to semiquantita-
tively deduce some of the relevant steps associated with oxidation.
Within the depth of DRIFT response the aromatic (e) and aliphatic
(f,g,h) hydrogen content is essentially depleted and there is a marked
increase in carbonyl content ranging from aldehydes/ketones (k) to the
more oxygen rich acid anhydrides (i,j). These oxygen insertion pre-
cursors to gaseous carbon dioxide give rise to spectral intensities
which actually exceed that of the omnipresent polynuclear aromatic (l)
and methylene/ether (m,n,o) crosslinks. All of this is noted to have
little effect on the oxy-hydrogen phenolic, alcoholic and acid entities
that are present in various states of hydrogen bonding and gives rise
to the broad absorption feature (3600 to 2000 cm-1). A very rich and
enticing potpourri of potentially valuable information to say the
least.
One can note the limited penetration involved in DRIFT studies and
also note that the oxygen attack involves a layer of material near
the surface. Reabrasion of the same area of the same sample gives
rise to DRIFT spectrum E of Figure 2 where we note the reversion to
the spectral state so classically characteristic of the original coal.
The hydrocarbon bands (e,f,g,h) are again prominent and the carbonyl
bands (i,j,k) are greatly diminished indicating that there probably
existed a gradient of oxygen density which "tailed" beyond the approx-
imately 50 micrometers removed in the second abrasion. All of the
spectral features of E are somewhat enhanced with respect to C due to
an increase in DRIFT efficiency brought about by a more enhanced
roughness and/or a modified refractive index due to loss of infrared
inactive graphitic carbon during the combustion phase of this study.
Future studies with thinner sectioning will allow us to obtain further
details from a detailed and quantititive analysis of the chemical and
stuctural profile of the steady state oxygen insertion/diffusion
process.

To this end we have instigated a program to quantitatively analyze our
DRIFT spectra. The problem is complex since virtually every band over-
laps one or more adjacent bands. There is currently a strong inter-
national move to quantitatively analyze infrared spectra in general
{16.17,18,19} and coal spectra in particular{6,7} using sophisticated
and readily available computers{20}. Figure 3 is our analysis of the
data of DRIFT spectrum E, using the second derivative to rather ac-
curately assess the frequencies of the individual contributing absorp-
tion bands in terms of the resultant inflection points in the sum-
mation composite. The results compare favorably with those of Painter
et. al.{7}. There has been a renewed interest in "resolution enhance-
ment" of spectra by deconvolution{21} techniques now that fast Fourier
transforms are available and the required algorithms have been
developed. Griffiths et.al.{9} have been able to accurately position
coal structure bands with Fourier self deconvolution of their spectra.
Our results are give in Figure 4 for the hydrocarbon region of DRIFT
spectrum E shown with the Fourier self-deconvolution. Comparison of
Figures 3 and 4 merely point out the close relationship between decon-
volution and derivatization in terms of the multiplicative operation
that corresponds to each in the time domain{22,23}. Both operations
are mathematically classed as filter functions (albeit negative or
"unsmoothing" filters in this instance){24}. The prime utility of
both techniques is to accurately measure characteristic band
frequencies without the human error associated with locating inflect-
ion points and "shoulders" reliably and reproducibly. That goal is
achieved admirably in both cases. It is now such a simple task that
we can turn it over to the simple "mind" of the computer where the
maxima in both curves are evaluated without human intervention or bias.
Table 1 tabulates the band position for our analyses compared to the
results of others{25,26}. These carbon-hydrogen stretching frequencies
are ideally suited to test our program since they are relatively im-
mune to substituent and environmental effects{25}.

Quantitative analyses requires accurate evaluation of the intensity
(height), integrated area and/or band width of the bands associated
with the vibration of each entity. This can be done most reliably by
iterative minimum least squares{16,17} or some related technique in
which the summation of the composite peaks most closely matches the
experimental spectrum. The band positions from the second derivative
and/or Fourier self-deconvolution are used as first approximations and
intensities are estimated ratiometrically (utilizing the area conserva-
tion inherent in deconvolution). Initial band widths are taken to be
the optimum value (average) used in the Fourier self-deconvolution.
Generally the iterations converge in 6 to 10 steps without divergence,
which can occur if initial estimates are grossly disparate from the
optimum value. Our results are given in Figure 5 where we note that
the deviation (upper line) is at or near the signal/noise ratio of the
experimental spectrum. When this case prevails (standard deviation
approximately equals the signal/noise ratio) for the converged inter-
ations there is no justification of further deconvolution and/or
incorporation of additional bands in the envelope. Conversely, more
stringent deconvolution is not warranted if the standard deviation is
not appreciably diminished toward the signal/noise ratio. These

3

techniques are readily implemented with the aid of today's computers
and we must be cautious that we do not abuse them by taking them
beyond their limits.

The broad band due to the oxygen-hydrogen stretching vibrations is
seen to be composed of 5 bands whose intensities and widths are given
in Figure 6. The positions and widths of these bands closely match
those of Solomon et. al.(6). Our spectrum is taken in vacuum (.00002
torr) and is a true vacuum spectrum as compared to the purge state
that is approached when alkali halide pellets are allowed to equili-
brate. It is readily noted that the five frequencies are associated
with successively stronger hydrogen bonding (27,28,29). The relative
strengths are due to higher degrees of coordination between that of a
linear bond to that of the 5 fold interaction of cubic close packing
of the acceptor ligands oriented somewhat symmetrically around the
donor hydrogen of the covalent phenol, alcohol, or acidic entities.
Intermediate states correspond to lesser interactions with hydrogen.
Each band corresponds to increased O-H length, decreased O-H...O
separation, increased bandwidth, and enhanced extinction coefficient
in accordance with known behavior of similar hydrogen bonding(27-29).
The importance in a good understanding of these hydrogen bonds is
essential to understanding the structure and chemistry and structure
of coals and related materials. More detail will be given in the oral
presentation.

The utility of this computer aided analysis is quite evident when
applied to the lower frequency range (Figure 8) where classical methods
based on visual observation and operator judgement are far from
quantitative. For example, the carbonyl bands at 1843, 1760 and 1720
cm-1 are readily resolved even in the presence of the very large
aromatic peak at 1608 cm-1(9). More details will be given in the oral
presentation to note the quantitative aspects of analyzing successive
spectra to elucidate the mechanism of oxidation of coals and chars.

CONCLUSIONS
Modern spectrometers with computer aided data aquisition and proces-
sing are very well suited to obtain diffuse reflectance infrared
spectra of coals with a minimum time and effort for sample preparation.
The spectra are of high caliber and are very comparable to the best
transmission spectra. Quantitative data is obtained for the region
penetrated by the incident beam. Depth profiling is possible utiliz-
ing this surface sensitivity of the DRIFT technique. Lateral scanning
is also possible to allow one to evaluate the heterogeneity and specie
distribution in the plane of the surface. The utility of DRIFT
techniques, so well recognized for powdered coals, can be used on
consolidated coals and thus measure and map chemistry and structure of
of the original coalified matrix. These studies are easily effected
under controlled environments to maintain coal bed conditions (high
relative humidity), generate inert atmospheres (nitrogen or argon
gas), induce and montior reactions (hydration/dehydration, oxidation,
hydrogenation, carbonation ,etc.), or virtually any combination over a
wide range of temperatures (77 K to 800 K) and pressures (.00002 torr
to 2000 torr) with our present cell. All of the studies are easily
made free of matrix and supports normally used for IR studies of

4

solids. The high quality of the spectra are well suited to
quantitative analyses using modern computer aided deconvolution and
related composite band evaluation techniques. We now can start to
evaluate the complex chemistry and structure of coals and related
materials and to follow the fate of each and every specie as we obtain
spectra under realistic conditions of coalification and subsequent
combustion or processing for fuels and feedstocks.

REFERENCES
1. N. R. Smyrl and E. L. Fuller, Jr., "Chemistry and Structure of
Coals: Diffuse Reflectance Infrared Transform (DRIFT) Spectroscopy of
Air Oxidation." in "Coal and Coal Products: Analytical Character-
ization Techniques" edited by E. L. Fuller, Jr., American Chemical
Society, 1982.
2. E. L. Fuller, Jr., N. R. Smyrl, R. W. Smithwick, and C. S. Daw,
"Chemistry and Structure of Coals: Air Oxidation Related to Fluidized
Bed Combustion", Preprints, Div. Fuel Chem. A.C.S., 28, 44(1983).
3. M. P. Fuller and P. R. Griffiths, Anal. Chem. 50,1906 (1978).
4. D. W. van Krevelen, "Coal", Elsevier Publ., 1961.
5. Robert S. McDonald "Review: Infrared Spectrometry", Anal. Chem.
54, 1250, (1982).
6. P. R. Solomon, D. G. Hamblen and R. M. Carangelo, "Applications of
Fourier Transform Spectroscopy Infrared Spectroscopy in Fuel Science",
in "Coal and Coal Products: Analytical Characterization Techniques",
edited by E. L. Fuller, Jr., American Chemical Society, 1982.
7. Paul C. Painter, Randy M. Snyder, Michael Starsinic, Michael Coleman,
Deborah W. Kuehn, and Alan Davis, "Fourier Transform Infrared
Spectroscopy: Application to the Quantitative Determination of Functional
Groups in Coal", ibid., 1982.
8. Peter R. Griffiths and Michael P. Fuller, "Mid-infrared Spectrometry
of Powdered Samples" in "Advances in Infrared and Raman Spectroscopy"
Vol. 9, p. 63, edited by R. J. H. Clark and R. E. Hester, Heyden and
Sons, 1982.
9. Peter R. Griffiths, Shih-Hsien Wang, Issam M. Hamadeh, Paul W. Yang
and David E. Henry, "Direct Investigation of Reacting Coals by Diffuse
Reflectance Infrared Spectroscopy", Preprints, Division of Fuel
Chemistry, A.C.S. 28, 27 (1983).
10. N. R. Smyrl, E. L. Fuller, Jr., and G. L. Powell, Applied
Spectroscopy 37, 38 (1983).
11. E. L. Fuller, Jr., N. R. Smyrl, J. B. Condon and M. Eager,
J. Nuclear Materials, IN PRESS(1983).
12. E. L. Fuller, Jr., J. Colloid and Interface Science 75, 577 (1980)
13. E. L. Fuller, Jr., J. Colloid and Interface Science 89, 309 (1982)
14. W. W. Wendtlandt and H. G. Hecht, "Reflectance Spectroscopy",
Interscience Publ., 1966
15. F. A. Jenkens and H. E. White, "Fundamentals of Optics", McGraw-
Hill, 1957.
16. R. D. B. Fraser and E. Suzuki, Anal. Chem.,38,1770 (1966)
17. R. D. B. Fraser and E. Suzuki, Anal. Chem.,39,37 (1969)
18. R. N. Jones and K. Shimokoshi, Applied Spectroscopy, 37, 59 (1983)
19. P. H. Von Cittert, Z. Phys., 69, 298 (1931).
20. R. Peter Young, "Computer Systems", in "Infrared and Raman
Spectroscopy" edited by E. G. Brame, Jr., and J. G. Grasselli,
Marcel Dekker, 1977.

21. W. E. Blass and G. W. Halsey, "Deconvolution of Absorption Spectra", Academic Press, 1981.
22. J. K. Kaupinen, D. J. Moffat, H. H. Mantsch and D. G. Cameron, Anal. Chem. 53, 1454 (1981)
23. R. E. Ziemer and W. H. Tranter, "Principles of Communications", Houghton Mifflin, 1976.
24. J. K. Kaupinen, D. J. Moffat, D/ G/ Cameron and H. H. Mantsch, Applied Optics 20, 1866 (1981).
25. Norman B. Colthup, Lawrence H. Daly, and Stephen E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press,1964
26. Herman A. Szymanski, "IR: Theory and Practice of Infrared Spectroscopy", Plenum Press, 1964.
27. George C. McClellen and A. McClellan, "The Hydrogen Bond", W. H. Freeman, 1960.
28. Serge N. Vinogradov and Robert H. Linnell, "Hydrogen Bonding", Vand Nostrand Reinhold, 1971.
29. Walter C. Hamilton and James A. Ibers, "Hydrogen Bonding in Solids", W. A. Benjamin, 1968.

TABLE 1. VIBRATIONAL FREQUENCIES EVALUATED FOR KENTUCKY #9(58) COAL
(freqencies tabulated as wavenumbers, cm-1)

This work	Ref. 7	Ref 25----------Assignment	
3051	-----	3050+/-50	Ar-H
3017	-----	3025+/-25	R2C=CHR & RCH=CHR
2958	2956	2962+/-10	RCH3
2925	2923	2925+/- 5	ArCH3 & R2CH2
2894	2891	2900+/- ?	R3CH
2870	2864	2872+/-10	RCH3 & ArCH3
2854	2849	2855+/-10	R2CH2
2752	-----	2732+/-12	RCHO

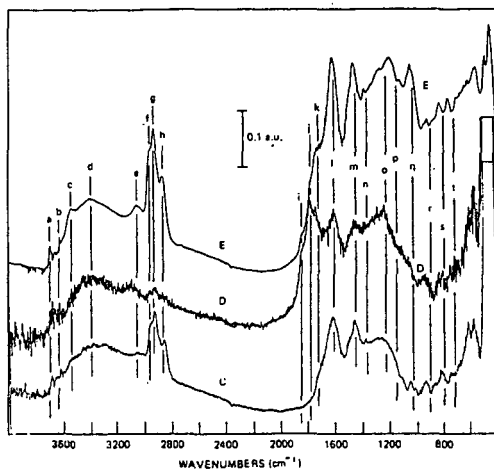DRIFT SPECTRA: MODIFIED KENTUCKY NUMBER NINE

Figure 2. Effects of Chemical and Physical Treatment of Kentucky #9

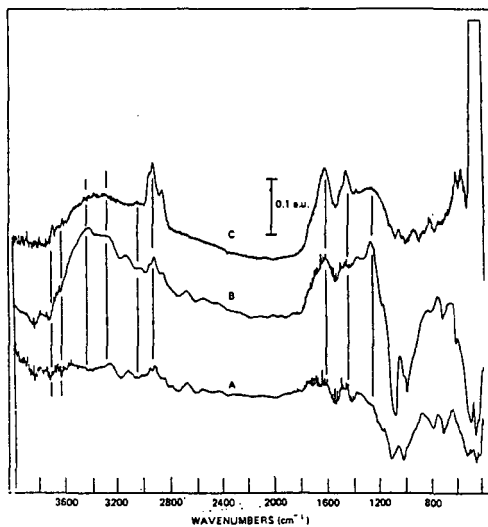REFLECTANCE SPECTRA: SOLID KENTUCKY NUMBER NINE

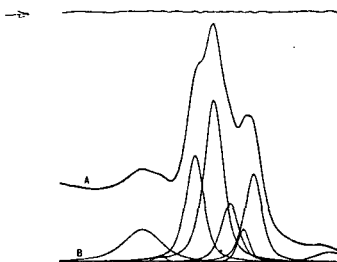Figure 1. DRIFT Spectral Variation for Kentucky #9

7

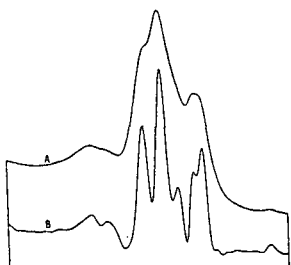Figure 5. Least Squares Composite Sum for
Hydrocarbon (K958)

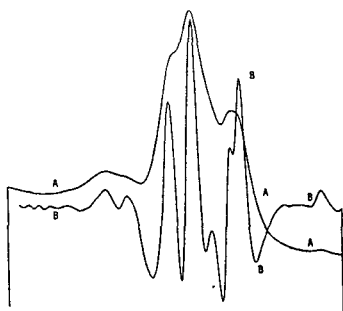Figure 4. Fourier Self-deconvolution of
Hydrocarbon Spectrum (K958)

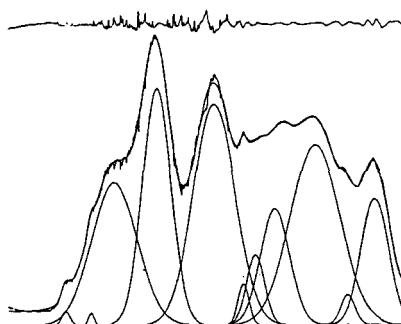Figure 3. Second Derivative Analysis of Hydrocarbon
Spectra (K958)

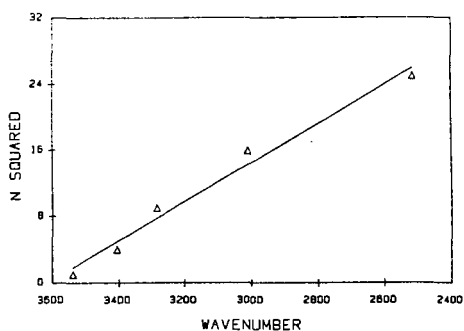Figure 8. Least Squares Composite Sum for Low Frequency Bands (K958)

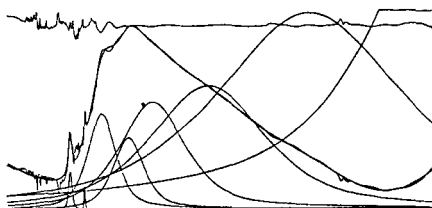Figure 7. Hydrogen Bonded Hydroxyl Sequence Variation (K958)

Figure 6. Least Squares Composite Sum for Hydroxyl Bands (K958)

9